2515

ALKENYL SUCCINIC ACID-SILICONE SYSTEMS FOR WATER-RESISTANT LEATHER*

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ABSTRACT

A study was conducted on making water-resistant leather from chrome and chrome-glutaraldehyde-retanned stock lubricated using a fatliquoring system based on alkenyl succinic acid in an aqueous tetrahydrofurfuryl alcohol system. The degree of water resistance imparted after treatment with a high level and low level of Dow-Corning 1109 Resin‡ dissolved in tetrachloroethylene was evaluated by measuring flex values on a Dow-Corning Leather Tester.‡ In general, fatliquoring with an alkenyl succinic acid and retannage of the chrome sides with glutaraldehyde improved the leather as a substrate for silicone treatment and improved the efficiency of the silicone.

INTRODUCTION

The leather industry at present is utilizing processes based on silicones, chrome salts of perfluoro acids, alkenyl succinic acid and stearato chromic chloride to make leather resistant to water penetration. Various products of these types are available. These treatments, however, have not found extensive use for one reason or another. Some, for example, silicones and fluorochemicals, are relatively expensive. Studies were undertaken at this laboratory in order to develop more economical procedures for imparting to leathers resistance to water penetration. In a symposium on waterproofing held recently (1) it was established that several factors would contribute to the effectiveness of a water-resistant system. It was suggested that the fat content should be kept to a five percent level and that the types of fatliquor used be emulsified oils or solvent base fatliquors. Highly sulfated oils tend to act as wetting agents and could have a decided detrimental influence on water resistance.

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Dr. George von Fuchs (2, 3, 4, 5) discovered that alkenyl succinic acid (ASA) was not only a water-repellent compound but that it was also an excellent leather lubricant even when used in small amounts. Neher and collaborators (6, 7) further studied alkenyl succinic acids to gain an insight to the mechanism of their action. Because of their efficient lubrication at low concentration, it appeared that the alkenyl succinic acids offered considerable promise as lubricants for preparing leathers to be given water-repellent treatments in general and may not be limited necessarily to ASA as the water-repellent treatment.

The present study to determine the compatibility of alkenyl succinic acid lubrication with other water-repellent materials was stimulated by the development in our laboratory of a practical process for fatliquoring with alkenyl succinic acids (8). This paper reports an evaluation of several factors regarding their influence on water resistance of leathers treated with silicones. Factors of particular interest included the use of an alkenyl succinic acid in a drum fatliquoring process and the influence of a glutaraldehyde retannage of chrome stock.

EXPERIMENTAL

Stock.—The sides used in the following experiments were commercially-tanned, chrome-grain splits, 5–6 oz., soaked back by drumming in water for 30 minutes and drained. The shrinkage temperature (Ts) in water in a pressure apparatus (9, 10) was 107°C. (225°F.). In order to study the effect of a glutaraldehyde retannage of the chrome-tanned stock, the sides were retanned with five to 10 percent (based on blue weight) glutaraldehyde (25 percent solution) for two hours at an average temperature of about 130°F. according to procedures recommended in publications from our laboratory (11). The Ts of the retanned leather, determined in water (9, 10), was 110°C. (230°F.).

Fatliquoring.—The tanned stock was drained and fatliquored in a drum with an alkenyl succinic acid (Casyl 18) by the procedure developed at our laboratory (8). This procedure (percentage based on blue weight), outlined briefly, follows:

Emulsify (Ref. 8):

Casyl 18	1%
Tetrahydrofurfuryl alcohol	5–10%
Water	40%

Warm to 120°F.

Add: Tanned stock at 120°F.

Drum for 0.5 to 1.0 hour; fatliquor exhausts readily and completely.

Horse overnight, then air dry.

The crusted stock was sammied and staked by conventional procedures at a nearby side leather tannery.

Silicone Treatment.—The leather that was lubricated, dried and staked as described above was treated with Dow-Corning 1109 Resin dissolved in tetrachloroethylene to give two levels of silicone concentration:

High Level.—The sides were pulled through a bath containing six percent of the silicone in tetrachloroethylene resulting in an uptake of 11.8 percent silicone on the dry leather basis.

Low Level.—A chrome side retanned with glutaraldehyde was pulled through a bath containing four percent of the silicone in tetrachloroethylene resulting in an uptake of 5.9 percent silicone on the dry leather basis, about half of that obtained in the high-level treatment described above.

Evaluation of Treated Leathers.—After air drying for several days the sides were blocked into 4″ x 4″ pieces taken from the bend, shoulder, and flank areas, as shown in Figure 1. Randomized selections were taken from these areas with selections from each side being approximately in the same sampling position. The selected samples were then evaluated for resistance to water penetration by a dynamic flex test, as described by previous investigators concerned with water-resistant side leathers (12). The number of flexes on the Dow-Corning Leather Tester to the first penetration of water (electronic end point) was used as a criterion of the effectiveness of the treatment.

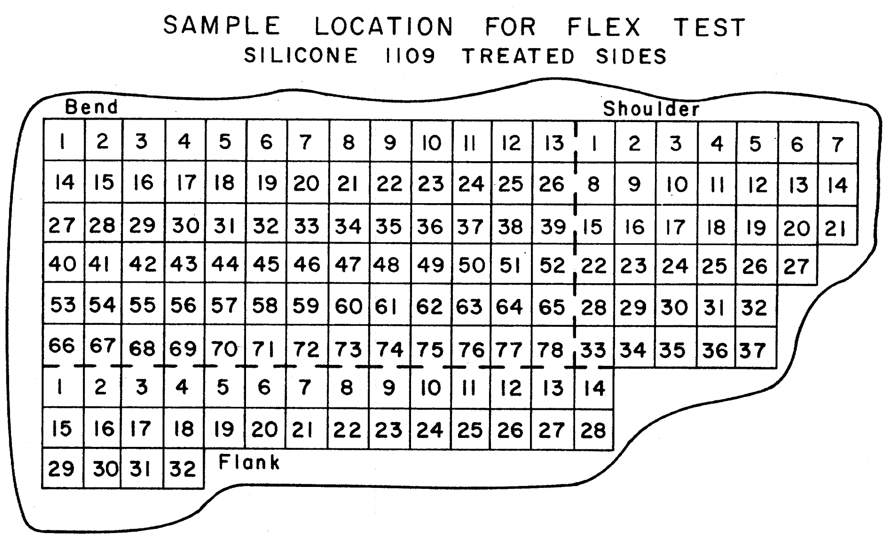

FIGURE 1.—Sampling positions of silicone treated sides taken for flex test.

For purposes of comparison, some of the sides were sent to a tanner and given commercial fatliquor and silicone treatments. These data are summarized in Tables I and II and in Figure 2.

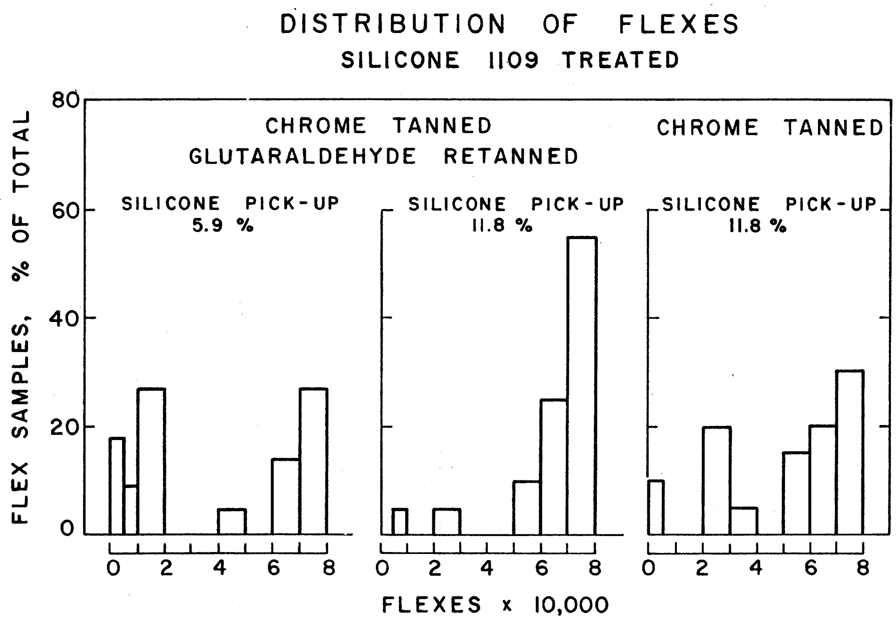

FIGURE 2.—Distribution of flexes from silicone treated sides. The histograms are weighted on the low side since the measurements on a number of samples were terminated before failure. Those terminated in the 60,000 to 70,000 range were included with those that failed in this range. All samples with values above 70,000 were counted with those that failed in the 70,000 to 80,000 range.

Other physical properties (Table II) of the water-resistant leathers were determined by standard ALCA methods.

DISCUSSION OF RESULTS

As shown in a previous publication (8), certain polar water-soluble organic substances, i.e., tetrahydrofurfuryl alcohol, are excellent solvents for alkenyl succinic acid, and oil-in-water emulsions could be formed easily with low concentrations of alkenyl succinic acid alone or in the presence of raw oils. These emulsions were rapidly exhausted under ordinary fatliquoring procedures and gave leather substrates that appeared comparable to those lubricated by a dipping technique recommended by von Fuchs (2–5). This new procedure was a decidedly improved technique from the practical standpoint for effecting lubrication with an alkenyl succinic acid. This procedure avoided the use of emulsifying and wetting agents, and hence, it was important to evaluate this fatliquoring process as a means of lubricating leather for a water-resistant treatment, particularly silicones.

According to Morgan (13), in order to get good water resistance with silicones in a solvent system, it was necessary to dip in a solution containing at least ten percent and preferably fifteen percent of the actual polymer. This gave an uptake of about five to ten percent of actual silicone on the leather weight, which is several times the amount required to coat the leather fibers completely. Morgan also pointed out that lower treatment levels might prove to be quite satisfactory, and adequate results from a practical standpoint might be obtained with possibly no more than one to two percent silicone. With this in mind, two levels of a silicone solvent dip system were used to attain a high and low level of silicone in the leather.

Flex values to initial water penetration obtained on leathers that were treated with alkenyl succinic acid and silicone at two levels are shown in Table I: Flex values are shown for each sampled position and these reveal the extreme variability throughout the side. Hebert (14), in his study on water resistance testers, had found a large scatter of flex values and had attributed premature failures to poor anchorage of the polymer in the leather fibers. A weak point or a defect in the side can also cause a premature breakdown and activation of the electronic signal. The values shown in Table I range from 985 to 237,000 flexes for samples taken from the bend, from 4,475 to 106,900 flexes for samples from the shoulder, and 7,144 to 250,500 flexes for samples from the flank area. These are similar in range to the results obtained by Hebert. It will be noted that many specimens resisted water penetration even after 100,000 or more flexes which required running the test for several days. To expedite testing, it was subsequently decided to cut off samples at about 60,000 flexes which is equivalent to an over-night test.

The distribution of flex values and the percentage of specimens that failed at the different levels of flexing is shown by the histogram, Figure 2. As far as is known, no definite value or range of values has been set to establish an acceptable level for water-resistant leather although a figure of 4,000 flexes in the past has been generally considered as a minimum for suitable water-repellent treatments. However, this figure presumably was obtained from the testing of finished leather. It has been suggested that in order to arrive at an acceptable value, the unfinished leather flexes must be substantially higher. A flex value of 20,000 has been suggested as being desirable to insure good protection in footwear.** From the graph, it is observed that in the case of the chrome side retanned with glutaraldehyde at the lower level of silicone treatment, 54 percent of the total specimens tested fell in the 0–20,000 flex range, the lowest value being 985 flexes. This latter result could very well have been caused by poor distribution of the polymer or a slight defect in the specimen itself. At the high-level silicone treatment of chrome stock retanned with glutaraldehyde, only five percent of the values fell in the range of 0–20,000 flexes.

On the other hand, when the chrome side treated at a high-level silicone was compared to the high-level treatment of the glutaraldehyde-retanned stock, the latter showed the greater resistance to water penetration with 90 percent of the

**Acceptable level for unfinished leather suggested by a reviewer.

samples testing well above the 50,000 flex value, as compared to only 65 percent of the samples taken from the chrome stock. In comparing the high- versus the low-level silicone treatment of the chrome side retanned with glutaraldehyde, as might be expected, the high-level treatment gave a higher degree of water resistance since, for the low-level silicone treatment, only 41 percent of the samples flexed at 50,000 or more.

TABLE I

POSITION AND FLEX VALUES* OF SAMPLES FROM SILICONE TREATED SIDES

Bend		Shoulder		Flank	
Position	Flexes	Position	Flexes	Position	Flexes
		Chrome-glutaraldehyde retanned side, 5.9% silicone			
13	11660	3	8470	2	44465
14	4760	8	15335	8	66042
31	2246	14	4475	12	7144
35	> 77762	17	19010	19	66290
40	14620	22	11608	28	72390
50	> 77762	32	> 77272	29	100678
65	10010	33	> 71725		
69	985				
76	69600				
		Chrome-glutaraldehyde retanned side, 11.8% silicone			
13	5068	11	51700	5	> 83125
14	76530	15	106903	12	250535
30	109366	21	26545	15	> 83125
34	> 67000	24	55360	24	> 79977
52	237136	33	> 88600	30	> 61744
61	> 67000	36	> 88600	32	> 61744
68	> 88600				
76	> 61774				
		Chrome-tanned side, 11.8% silicone			
13	54291	3	20502	3	29660
14	> 67079	8	21222	5	67537
30	> 77482	14	5000	13	66066
34	52854	17	4517	20	69134
40	> 77710	33	> 79977	26	20926
52	76712	37	58872	30	> 78357
68	34657				
78	> 77710				

*Values obtained from Dow-Corning Leather Tester.

From the data presented, the water resistance of the chrome side with the high-level treatment, was comparable to the low-level silicone treatment of the

TABLE II

COMPARISON OF PHYSICAL PROPERTIES OF THE LEATHERS

Treatment		Chrome				Glutaraldehyde-retanned			
Fatliquor	Silicone	Tensile* psi	Slit Tear* lb.	Grain Crack† lb.	Flexes‡	Tensile* psi	Slit Tear* lb.	Grain Crack† lb.	Flexes‡
Commercial**	Full Strength**	2340	32	280	19285	3620	35	450	>178000
"	½ Strength**	3160	36	275	8080	3380	34	360	7920
Alkenyl Succinic Acid	Full Strength**	2560	28	300	161870	2220	27	470	>178000
"	½ Strength**	3445	25	510	4350	3190	28	510	>178000
Alkenyl Succinic Acid	6% Silicone Dip††	1800	25	250	291600	1940	23	430	178000
"	3% Silicone Dip‡‡	1400	17	200	45700	2430	20	360	33000

*Average of three tests.
†Test on one sample only.
‡Average of two tests.
**Composition used by cooperating tanner in his normal production.
††Chrome side-silicone uptake 10.2%; glutaraldehyde-retanned side-silicone uptake 10.8%.
‡‡Chrome side-silicone uptake 5.4%; glutaraldehyde-retanned side-silicone uptake 6.4%.

glutaraldehyde-retanned stock. It can also be assumed from the data that a glutaraldehyde retannage will give a substrate that will show improved resistance to water penetration under dynamic conditions.

To confirm these encouraging results, a larger scale test was undertaken. Twelve chrome-tanned sides were procured from a tannery in the blue shaved state. Six of these sides were retanned with ten percent glutaraldehyde (25 percent solution) for two hours at an elevated temperature. Half of the glutaraldehyde used for retannage was fixed by the sides in this period of time. Two of the chrome sides and two of the glutaraldehyde-retanned sides were processed at a tannery with a regular production run using a commercial fatliquor and treating with a water-repellent system full-strength and half-strength as used commercially. Two of the chrome and two of the glutaraldehyde-retanned stock were fatliquored in a drum with the experimental system using one percent alkenyl succinic acid. These sides were then processed commercially and given a full-strength or half-strength treatment with water-repellent material. The remaining sides were fatliquored with the experimental system (one percent ASA) and the water repellent applied by pulling through a three percent and six percent solution of silicone in tetrachloroethylene with approximate uptakes of six percent and 10.5 percent silicone.

Physical tests were made on samples taken from the "W" position. From the data presented in Table II, it is observed that generally the chrome sides retanned with glutaraldehyde show higher values for tensile and grain crack as well as water resistance. Slit tear values were essentially the same for both types of leathers. A trend to higher flex values was obtained from chrome sides retanned with glutaraldehyde when the substrate was lubricated by a commercial fatliquoring system. Highest flex values were obtained for the experimental alkenyl succinic acid fatliquor and silicone treatment when applied to chrome stock and glutaraldehyde-retanned stock but perhaps at a sacrifice of other leather characteristics. Evaluation of these sides ranked them as follows: The chrome side treated with a three percent silicone solution was found to be best for tightness of break and had good temper. Next in order was the chrome side dipped in a six percent silicone solution, which had fairly good break but was slightly crusty. The retanned sides were third and fourth in preference since they showed a poorer break and had a softer feel. It is conceivable that this latter defect might be corrected by using a smaller amount of the alkenyl succinic acid.

CONCLUSION

The use of alkenyl succinic acid in a drum fatliquoring system has produced a leather substrate that is quite receptive to a silicone water repellent system. The amounts of silicone used can be substantially reduced with no adverse affects on the flex values as obtained. Although the present level of treatments proposed are only for comparison, lower treatment levels may prove to be quite satisfactory. Since high flex values to initial water penetration were obtained in this relatively severe dynamic test method it seems likely that a lower level of silicone treatment will give a leather with acceptable water resistance. Glutaraldehyde retannage of chrome stock has also aided in producing a substrate more receptive to water repellent treatments.

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